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1. REPORT DATE (DD-MM-YYYY) 30-12-2011		2. REPORT TYPE Performance/Technical Report (Monthly)		3. DATES COVERED (From - To) 12/30/2011 - 1/24/2012		
4. TITLE AND SUBTITLE Polyfibroblast: A Self-Healing and Galvanic Protection Additive				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER N00014-09-1-0383		
				5c. PROGRAM ELEMENT NUMBER		
				5d. PROJECT NUMBER		
6. AUTHOR(S) Benkoski, Jason J.				5e. TASK NUMBER FGY25		
				5f. WORK UNIT NUMBER		
				8. PERFORMING ORGANIZATION REPORT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Johns Hopkins University Applied Physics Laboratory 11100 Johns Hopkins Rd Laurel, MD 20723				10. SPONSOR/MONITOR'S ACRONYM(S) ONR		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 875 North Randolph Street Arlington, VA 22203-1995				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
				12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for Public Release: distribution is Unlimited.		
13. SUPPLEMENTARY NOTES						
14. ABSTRACT The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.						
15. SUBJECT TERMS corrosion protection, self-healing, coatings, polymers						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT		18. NUMBER OF PAGES	
a. REPORT	b. ABSTRACT	c. THIS PAGE	UU		Jason J Benkoski	
U	U	U	6		19b. TELEPHONE NUMBER (Include area code) 240-228-5140	

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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #2

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Reporting Period: December 30, 2011 through January 24, 2012
Date of Report: January 24, 2012

20/20/26019

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1 Summary

In January, we primarily explored new formulations that would improve the speed of microcapsule synthesis, and we tested whether the surfactant drying method had unwanted side-effects on coating performance.

Increasing the temperature, but keeping it below the glass transition temperature of the polymer appears to be the most promising route to speeding the synthesis. The surfactant drying method did have a small but noticeable effect on wet adhesion that needs to be addressed moving forward.

2 Project Goals and Objectives

While we await additional funding and the establishment of a subcontract agreement, we will use our first \$30k allocation to improve the speed, cost, and scalability of our sample preparation protocol.

3 Key Accomplishments

3.1 Reaction Speed

A number of formulation changes were attempted to improve the reaction speed for the microencapsulation reaction. Currently, the microcapsules soak for 2-4 days prior to filtration to allow the shells to thicken. This method was adopted in order to avoid unwanted internal polymerization that occurred at 70°C. We hypothesized that the room temperature synthesis generated superior microcapsules because it took place below the glass transition temperature of the polymer shell (58°C).

Table I shows a sample of the reaction formulations that were tried. Generally speaking, none of the new formulations outperformed the current, best practice formulation. We attempted to increase the reactivity of the isocyanate monomer, decrease the size of the amine crosslinker, and increase the rigidity of the amine crosslinker (to increase the glass transition temperature). While we were able in some cases to grow thicker polymer skin layers more rapidly, the resulting shells were more brittle, which defeated the purpose of having the thicker shell to begin with.

So far the most promising method for decreasing the reaction time is to increase the temperature while taking care to stay below the glass transition temperature. Increasing the temperature to 35°C appears to increase the reaction speed without causing significant internal polymerization.

%In Silane Mixture, Added to 50g Gum Arabic						%In Silane Mixture, Balance to 50g Gum Arabic				Stir Time	Heat After Stir?	Processing Notes			
%Silane		%Monomers				%Crosslinkers						Appearance after 1 hour	Can be filtered after 24 hours?	Liquid Center	Loose Powder
OTS	MPTMS	IPDI	PPI	HMDI	TDI	DETA	PEI	ED	XD						
75					25	10		10		1hr	No	Brittle	No	X	X
75					25	15		5		1hr	No	Brittle	No	X	X
75					25	5		15		1hr	No	Brittle	No	X	X
50					50				20	1hr	No	Some odd shapes	Yes (4 days)	Little	Yes
50					50	10			10	1hr	No	Some odd shapes	Yes (4 days)	Little	Yes
50		40			10	16			4	1hr	No	Brittle shells appear fairly thick	Yes (4 days)	Yes	No
30		60	10			5	5			1hr	35°C 1hr	Shells are not quite egg-shell thick	Yes (3 days)	Yes	No
50		40			10		5		5	1hr	No	Some odd shapes	No	X	X
50		40			10		5	5		1hr	No	Weak shells	Yes	Yes	No
50		40			10		5	5		1hr	35°C 1hr	Stronger than non-heated sample	Yes	Yes	No
50		40			10	5	5			1hr	No	Weak shells	Yes (4 days)	Yes	No
50		40			10	5	5			1hr	35°C 1hr	Stronger than non-heated sample	Yes	Yes	No
50		35			15	5	5			1hr	No	Weak shells	Yes	Yes	No
50		35			15	5	5			1hr	35°C 1hr	Stronger than non-heated sample	Yes	Yes	No
50		25		10	15	5	5			1hr	35°C 1hr	Fairly strong shells; can be tracked when burst	Yes	Yes	No
50		25		10	15		5	5		1hr	35°C 1hr	Weak shells	Yes, but not well	Yes	No
50		30		10	10	5	5			30 min	35°C 1.5hr	More brittle than 1/17 batch	Yes	Yes	No

Table 1: List of experiments tried to improve the reaction speed for microcapsule formation.

3.2 Effects of Surfactant Drying Method on Performance

The surfactant drying method is a major improvement over freeze-drying. To recap, we have found that rinsing the microcapsules with surfactant solution during vacuum filtration makes it possible to obtain a free-flowing powder upon air-drying. While these free-flowing powders are excellent for making primers, we wanted to test whether the surfactant residue would have a negative impact on corrosion protection or adhesion. We therefore performed our standard moisture resistance test and compared it with data on a similar sample from last year.

Per MIL-P-26915 specification and with guidance from ASTM D870 and D1308, scratches were permitted to cure for 10 days and then individually immersed in separate 1000 mL beakers filled with ~750 mL of deionized (DI) water at 38°C for 24 hours. Upon removal, the panels were rinsed with water, blotted dry, and inspected for changes in appearance (blistering, cracking, etc.). The level of corrosion in each scratch was graded on a 0-4 scale, where 0 represents 100% rust and 4 represents no rust. The adhesion tape test (D3359) was repeated on the section of the panel that was immersed within one hour of removal. Each test panel was photographed pre- and post-evaluation to document its condition.

As can be seen in Figure 1 and 2, the corrosion protection was largely unaffected. Any differences between the new and old technique are likely due to the normal scatter of the data rather than some systematic effect. Generally speaking, the 30% octadecyltrimethoxy silane (OTS) microcapsules protect the 0.003 – 0.016 in. scratches best, but struggle to protect wider scratches (0.032 – 0.125 in.). Corrosion protection improves as the amount of zinc powder in the primer increases. This trend is typical for OTS-rich microcapsules.

The effects on adhesion were more problematic. The primer with pure microcapsules as the filler peeled completely away from the surface at the conclusion of the test. The panels with smaller fractions of microcapsule filler were less affected, presumably because of the lower concentrations of surfactant residue.

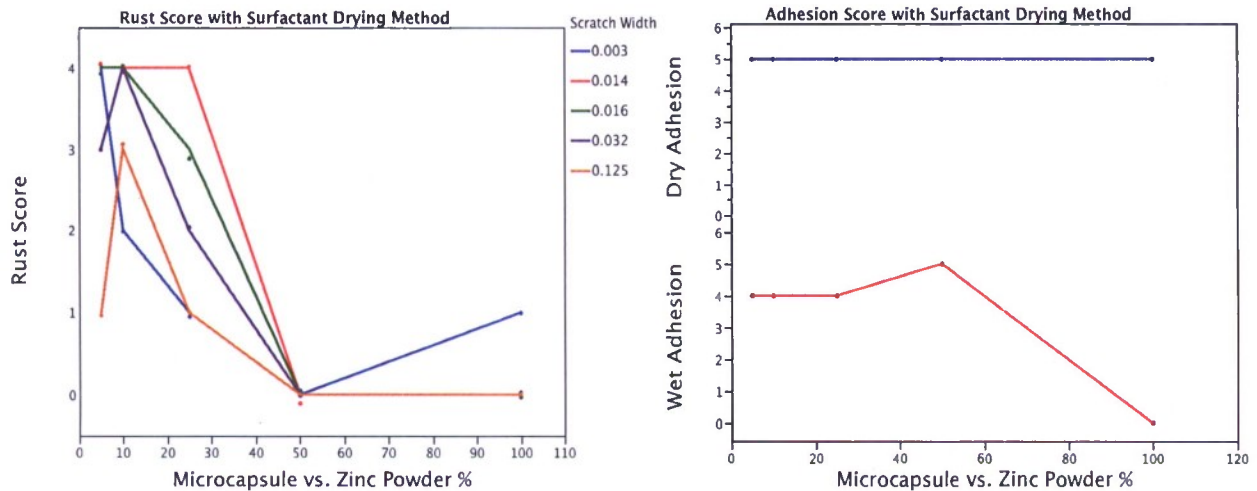


Figure 1: (left) Rust score for 30% OTS microcapsule primers dried in air after rinsing with surfactant solution according to modified ASTM moisture resistance test. A rust score of 4 corresponds to no rust, and a score of 0 indicates complete rusting across the scratch. (right) Dry adhesion score prior to water immersion, and wet adhesion post immersion for the same panels. Note that the rust score was best for narrower scratches and for higher Zn powder loading. The wet adhesion decreased sharply when the microcapsules comprised 100% of the primer filler (55% of the total primer by volume).

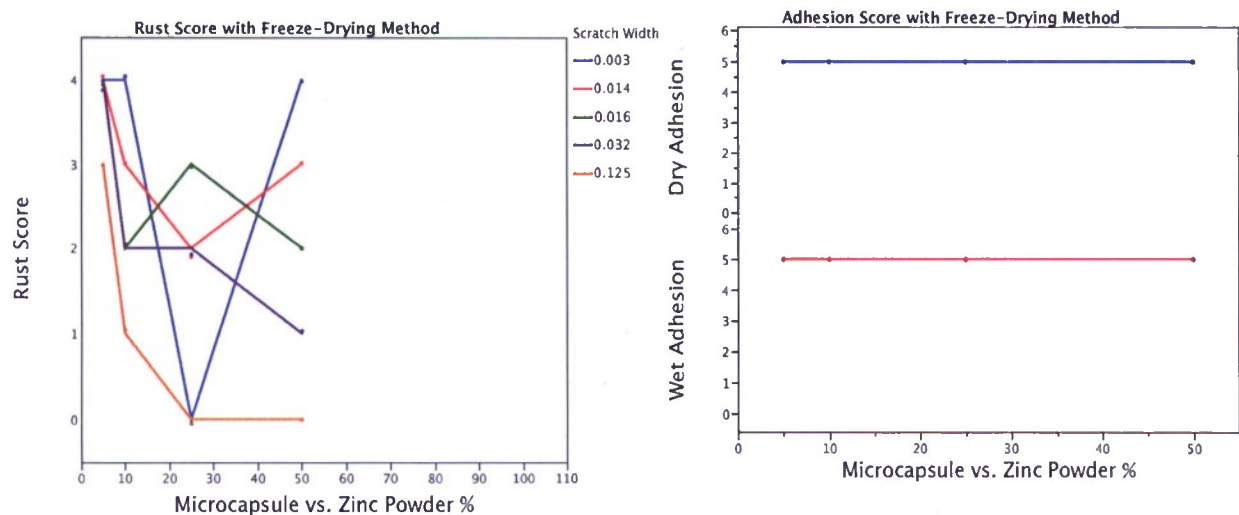


Figure 2: (left) Rust score for 25% OTS microcapsule primers dried by freeze-drying according to modified ASTM moisture resistance test. (right) Adhesion scores for the same. Although corrosion protection was similar to the surfactant drying method, the wet adhesion was much better.

4 Next Steps

4.1 Drying Method

Since the C12E4 surfactant caused a significant decrease in wet adhesion, we plan to investigate other anticaking agents such as higher molecular weight surfactants, oils, or water-soluble polymers.

4.2 Speed Improvements

Future attempts to increase the microencapsulation speed will explore the tradeoff between temperature and internal polymerization. Some internal polymerization can be tolerated so long as the overall volume fraction remains below about 5%. We may also investigate the use of organic solvents. We hypothesize that solvents such as chlorobenzene will temporarily soften the polymer shell to allow for faster diffusion of reactants across the interface. Continued heating and stirring would then allow the solvent to completely evaporate, leaving behind a hard polymer shell.